Chemical Geology 258 (2009) 327–337

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

# Intratest oxygen isotope variability in the planktonic foraminifer *N. pachyderma*: Real vs. apparent vital effects by ion microprobe

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ARTICLE INFO

*Article history:*
Received 25 July 2008
Received in revised form 23 October 2008
Accepted 23 October 2008

Editor: J. Fein

*Keywords:*
Foraminifera
Pachyderma
Oxygen isotopes
Vital effects
Ion microprobe
Calcite

ABSTRACT

Intratest oxygen isotope variations in the planktonic foraminifer *Neogloboquadrina pachyderma* sinistral (left coiling) from North Atlantic core top and multi-net samples were assessed by ion microprobe analysis from 2 to 6 μm spots with precision and accuracy better than 0.7‰ in $\delta^{18}O$ (2 SD). Within a single foraminiferal test from a core top sample comprising both ontogenetic calcite and outer crust, $\delta^{18}O$ values vary from 0.5‰ to 3.7‰ [PDB], exceeding the range of equilibrium $\delta^{18}O$ in the specimens' habitat by a factor of three. The isotopic difference between the ontogenetic calcite and the crust averages 1.8‰. Neither of the two types of foraminiferal calcite precipitates in equilibrium with ambient seawater. The ontogenetic calcite exhibits a negative vital effect $\Delta^{18}O_{(M\text{-}E)}$ ($\delta^{18}O_{(measured)} - \delta^{18}O_{(equilibrium)}$) ranging from −0.5 to −1‰. The largest negative fractionation is associated to the inner walls of juvenile chambers. In contrast, a positive vital effect of about 0.8‰ was observed in the crust with respect to the highest equilibrium $\delta^{18}O$ values at water depths below 200 m. Hence two vital effects that are opposite in sign are effective within a single foraminiferal test, indicating that 'whole test' values of this species are highly sensitive to the degree of encrustation and amplify or attenuate environmental signals. The negative vital effect of the ontogenetic calcite was verified by ion microprobe analysis of four nonencrusted net-sampled specimens reflecting three different depth intervals. Intra-ontogenetic oxygen isotope ratios in these juvenile tests range from 0.6 to 3.0‰ and exhibit a negative vital effect even larger than that observed in core top samples. Based on these data, the large range of 'apparent' vital effects reported for this foraminiferal species can be assessed by a mass balance calculation, assuming that the degree of encrustation is variable.



## 1. Introduction

Foraminifera are a successful group of amoeboid protists that invaded most marginal to fully marine environments in the course of the Phanerozoic. The oldest fossilized foraminifera are found in sediments of the earliest Cambrian (Goldstein, 2002). In modern oceans, they are the most diverse group of marine calcifiers. The shells (to be termed 'tests') of these unicellular organisms can be preserved in marine sediments for hundreds of millions of years, providing an important stratigraphic marker. Combined with their ubiquity in the marine environment, foraminifera are one of the most important chemical recorders of past environmental conditions. Since the pioneering study of Urey (1947) and subsequent analytical work by McCrea (1950), Epstein et al. (1951, 1953), and Emiliani (1966), the oxygen isotope composition of foraminiferal tests plays a pivotal role in palaeoceanography.

### 1.1. Foraminiferal vital effects

Ideally, the $\delta^{18}O$ value of foraminiferal calcite reflects isotopic equilibrium at the ambient temperature with local seawater, and thus foraminiferal calcite $\delta^{18}O$ is highly correlated with salinity and global ice volume. However, the fundamental problem of whether these organisms secrete $CaCO_3$ in isotopic equilibrium with ambient seawater is still a matter of debate. Any offset of foraminiferal calcite $\delta^{18}O$ from equilibrium diminishes the quality of paleoenvironmental reconstructions, unless this vital effect is accurately known. Unfortunately, a large range of apparent vital effects is found even in monospecific assemblages (Fig. 1) and nonequilibrium $\delta^{18}O$ values in planktonic foraminifera have never been adequately explained or calibrated (Rohling and Cooke, 2002). This problem is mainly attributed to the limitations of conventional analytical approaches that usually require multiple pooled tests in order to obtain one value of isotope ratio. Hence, valuable information regarding intratest heterogeneities is lost due to homogenization of samples. Consequently, a growing number of studies focus on the improvement of existing, and the development of supplementary, paleo-proxies often utilizing high resolution *in situ* techniques such as electron microprobe, laser ablation ICP-MS or ion microprobe (e.g. Nürnberg, 1995; Allison and Austin, 2003; Eggins et al., 2004; Sadekov et al., 2005). These high-

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doi:10.1016/j.chemgeo.2008.10.032

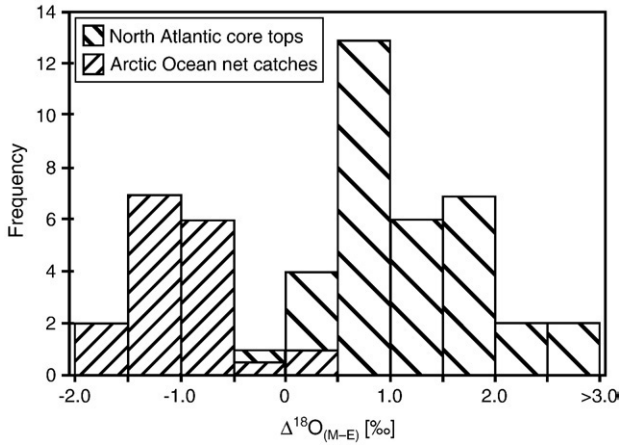


**Fig. 1.** Histogram showing the range of vital effects $\Delta^{18}O_{(M\text{-}E)}=\delta^{18}O_{(measured)}-\delta^{18}O_{(equilibrium)}$ in *N. pachyderma* (sin.). Core top data are from Wu and Hillaire-Marcel (1994) and references therein; net catch $\delta^{18}O$ values are published in Bauch (1997). Equilibrium values are calculated from the experiments of O'Neil et al. (1969) using temperature and ambient seawater $\delta^{18}O$ values given in the publications.

resolution studies have found significant intratest variability of the trace element distribution in foraminiferal calcite, indicating a strong biological control on the final test composition. In contrast, data for intratest $\delta^{18}O$ variations in foraminifera are very sparse because analysis at the appropriate scale has not previously been possible.

### 1.2. Foraminiferal life cycle and chamber formation

The majority of modern planktonic foraminiferal species migrate through the water column as part of their ontogenetic (juvenile to their mature form) development, adding new chambers and calcite layers at varying temperatures and salinities. Thereby, symbiont-bearing species are restricted to the euphotic zone, whereas symbiont-barren species can migrate below the euphotic level. For every newly secreted chamber, the whole pre-existing test is covered with a distinct layer of calcite (Fig. 2A, Reiss, 1957). This phase of test growth takes place at species specific dwelling depths within the upper 100 to 150 m of the water column above the pycnocline (Schiebel and Hemleben, 2005). Thus, each individual foraminiferal test is predicted to be isotopically zoned and to record a distinct growth history. This prediction is supported by previous studies demonstrating that repeated measurements of pooled foraminiferal tests by bulk acid dissolution from the same sample show significant variability of $\delta^{18}O$ beyond analytical uncertainty (Simstich, 1999). At the final phase of their life cycle, which usually ends after several weeks to months, some lamellar planktonic species wrap their entire crust in a thick calcite layer. In the tropical species, *Globigerinoides sacculifer*, this process is known to be associated with gametogenesis (Bé, 1980). The secretion of this final crust, which may contribute more than 50% of the total test weight in this foraminiferal species, takes place in water depths of up to several hundred meters (e.g. Duplessy et al., 1981). As a result, the final encrusted test of lamellar perforate foraminifera comprises two significantly different types of calcite: multilayered chamber walls secreted in the shallow waters above the pycnocline, termed the 'ontogenetic calcite', and a thick calcitic crust precipitated in deeper waters (Fig. 2A).

### 1.3. Degree of encrustation

Unfortunately, information is limited on variations in the degree of encrustation as well as the environmental parameters that initiate, intensify, or weaken this process. Available studies show contradictory results, indicating that the degree of encrustation as well as the proportion of encrusted specimens found in the sediment is highly variable. Arikawa (1983) estimated for the polar to subpolar planktonic foraminifer *Neogloboquadrina pachyderma* (sin.) (sinistral, left coiling) that the crust amounts to about 50% of the total test mass, whereas Stangeew (2001) reported that the crust accounted on average 63% of the total weight. Furthermore, Kohfeld et al. (1996) reported an increase in test weight of up to 80% during encrustation. Moreover, there is no clear-cut correlation between encrustation and ocean temperature. The down-core study of Srinivasan and Kennett (1974) revealed that the proportion of encrusted foraminiferal test is limited in the warmer episodes from the late Miocene to Recent, whereas Wu and Hillaire-Marcel (1994) hypothesized that the crust makes up only a small proportion of the total test weight for specimens living in surface water colder than 8 °C. Other authors established that the encrustation might be induced by low temperatures (Srinivasan and Kennett, 1974; Hemleben et al., 1989) whereas Stangeew (2001) found no correlation between temperature and the encrustation. Furthermore, Sautter (1998) reported no significant relation between the degree of encrustation and the bulk oxygen isotope ratio. In summary, despite the large number of studies using *N. pachyderma* (sin.) for paleoceanographic reconstructions, there is no consensus about (i) the variability in the degree of

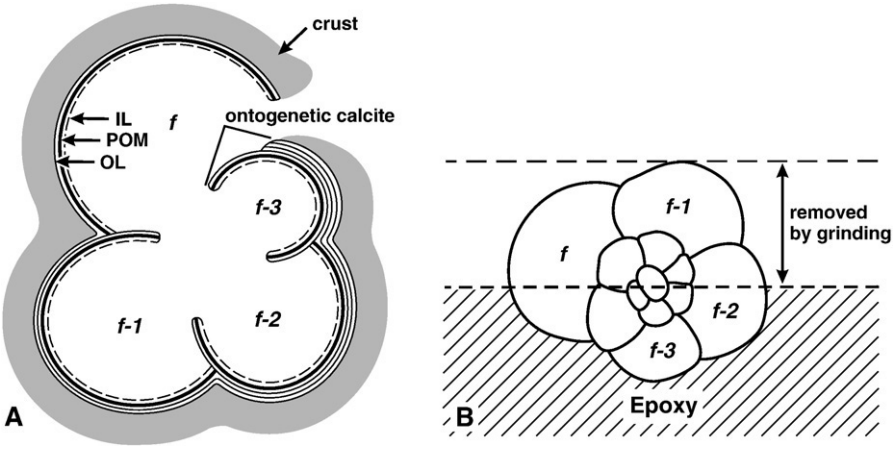


**Fig. 2.** A) Schematic illustration of the *N. pachyderma* (sin.) test microstructure of the final (*f*) and penultimate chambers (*f*-1 to *f*-3) of the last whorl (modified after Reiss, 1957). The average total number of chambers prior to reproduction is 15 (Berberich, 1996). The primary organic membrane (POM) is the site of initial calcification and probably serves as the template for calcite deposition (Hemleben et al., 1989). In bilamellar foraminifera, the POM has two active surfaces, one calcifying on the outer and the other on the inner side. The inside calcareous layer is termed the 'inner lining' (IL), while the outside calcareous layer is termed the 'outer lamella' (OL) (Hansen, 2002). Every time these organisms form a new chamber, their whole pre-existing test is covered with a new layer of calcite. The IL and OL are precipitated during the organisms' ontogenetic development and hence form the 'ontogenetic calcite' whereas the crust, which may contribute more than 70% of the total test weight in this foraminiferal species (Kohfeld et al., 1996), is secreted at the end of their life cycle. B) Spiral view of *N. pachyderma* (sin.) embedded in epoxy. The illustrated cross-section corresponds to polished surfaces in Figs. 4B and 6B.

encrustation (ii) whether low water temperature or other environmental parameters initiate, enhance or weaken the process of crust formation, (iii) the homogeneity of oxygen isotope ratios of different generations of calcite and (iv) the vital effects associated with the precipitation of the ontogenetic calcite and the outer crust.

This highly complex crust structure of planktonic foraminifera is both a blessing and a curse. On the one hand, the single oxygen isotope value obtained from conventional analytical approaches averages the whole life cycle, and using this value for reconstructing environmental conditions assumes one single, apparent calcification depth. Such data may be misleading and probably contribute to the large range of foraminiferal vital effects (Fig. 1). By simplifying the complex foraminiferal life cycle to one single value, incorrect estimates of temperature, salinity or depth are likely. On the other hand, using modern *in situ* analytical approaches, measurement of cross-sections of foraminiferal chamber walls provides a new proxy archive that can be regarded as a 'flight recorder' of a specimens' life cycle.

### 1.4. The $\delta^{18}O$ record in N. pachyderma (sin.)

In this paper, we report profiles of $\delta^{18}O$ across foraminiferal chamber walls from 2 to 6 μm diameter ion microprobe spots with a precision and accuracy of better than 0.7‰ (2 SD, spot-to-spot). Samples of the planktonic, polar to sub-polar foraminifer, *Neogloboquadrina pachyderma* sinistral, were obtained from a core top and a multi-net station from the North Atlantic Ocean (Fig. 3). We have selected this foraminiferal species for the following reasons. *N. pachyderma* (sin.) is asymbiotic, which eliminates the risk of additional variability in $\delta^{18}O$ as a result of symbiont activity during day/night cycles. In addition, this species belongs to the group of planktonic foraminifera that finalize their life cycle with the addition of a thick outer crust in water depths of up to several hundred meters (Kohfeld et al., 1996; Simstich et al., 2003). Consequently, at least two visibly different phases of calcite are present in core top samples of *N. pachyderma* (sin.), providing an excellent opportunity to evaluate the potential of *in situ* oxygen isotope measurements in foraminiferal calcite by ion microprobe. Furthermore, despite the large number of existing studies, the interpretation of $\delta^{18}O$ in tests of *N. pachyderma* (sin.) from paleo records is still challenging. Attenuation as well as amplification of environmental changes was reported based on values of $\delta^{18}O$ for this foraminiferal species. Bond et al. (1993) found that a shift in the abundance of *N. pachyderma* (sin.) from 80% to 100%, suggesting a temperature decrease of at least 6 °C (Imbrie and Kipp, 1971; CLIMAP, 1981), is accompanied by foraminiferal $\delta^{18}O$ values that suggest little or no change in temperature. On the other hand, glacial–interglacial fluctuations of $\delta^{18}O$ recorded in the calcite tests of this species have been reported to exceed 2.0‰ (Kellogg et al., 1978; Aksu et al., 1989; Hillaire-Marcel et al., 1989). This is nearly double the global average of the 1.0 to 1.3‰ change in the mean seawater $\delta^{18}O$ resulting from the built up and decay of the continental glacial sheets (Shackleton and Opdyke, 1973; Fairbanks, 1989). Based on these results, some researchers have suggested that the $\delta^{18}O$ of *N. pachyderma* (sin.) is biased by the partial record of local surface water changes in temperature, salinity or deglacial meltwater events

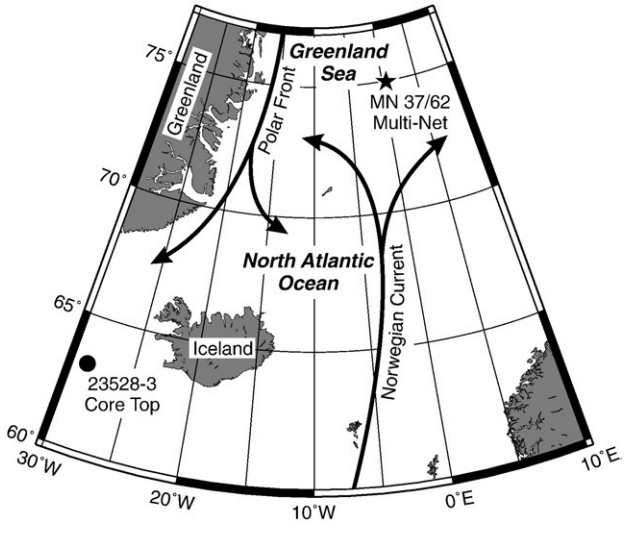


**Fig. 3.** Simplified surface hydrography of the North Atlantic Ocean and the Greenland Sea and the locations of the multi-net station and sediment surface (core top) sample.

**Table 1**
Oxygen isotope analyses of *N. pachyderma* (sin.) with 2 to 6 μm spot size by ion microprobe

| Sample and spot # | Sample spot position | $\delta^{18}O$ ‰ PDB | 2 SD[a] ‰ | $^{16}O$ cps×$10^6$ |
|---|---|---|---|---|
| Core top 23528-3; 63.16°N, 28.84°W, test #1 (Fig. 4) | | | | |
| Nps_43 #1 | Ontogenetic | 0.53 | 0.70 | 13.2 |
| Nps_43 #2 | Ontogenetic | 2.09 | 0.70 | 13.3 |
| Nps_43 #3 | Crust | 3.49 | 0.70 | 14.8 |
| Nps_43 #4 | Crust | 3.42 | 0.70 | 14.4 |
| Nps_43 #5 | Ontogenetic | 1.28 | 0.76 | 13.9 |
| Nps_43 #6 | Ontogenetic | 2.72 | 0.70 | 14.3 |
| Nps_43 #7 | Crust | 3.38 | 0.76 | 14.6 |
| Nps_43 #8 | Crust | 3.28 | 0.76 | 14.9 |
| Nps_43 #9 | Crust | 3.70 | 0.76 | 13.6 |
| Nps_43 #10 | Crust | 2.95 | 0.76 | 13.7 |
| Core top 23528-3; 63.16°N, 28.84°W, test #2 | | | | |
| Nps_44 #1 | Ontogenetic | 1.81 | 0.59 | 13.5 |
| Nps_44 #2 | Crust | 3.64 | 0.59 | 15.0 |
| Nps_44 #3 | Crust | 3.92 | 0.59 | 15.0 |
| Nps_44 #4 | Crust | 3.66 | 0.59 | 14.7 |
| Nps_44 #5 | Ontogenetic | 1.41 | 0.59 | 13.8 |
| Multi-net MN 37/62; 75°00N, 00.35°E. Sample interval 0 – 50 m (Fig. 6) | | | | |
| Nps_3 #1 | Inner ont. | 1.76 | 0.55 | 22.6 |
| Nps_3 #2 | Inner ont. | 1.58 | 0.55 | 21.4 |
| Nps_3 #3 | Outer ont. | 2.36 | 0.55 | 20.6 |
| Nps_3 #4 | Outer ont. | 2.17 | 0.55 | 21.1 |
| Nps_3 #5 | Outer ont. | 2.80 | 0.55 | 19.6 |
| Nps_3 #6 | Inner ont. | 1.42 | 0.76 | 21.0 |
| Nps_3 #7 | Inner ont. | 1.47 | 0.76 | 20.6 |
| Nps_3 #8 | Outer ont. | 2.42 | 0.76 | 20.6 |
| Nps_3 #9 | Outer ont. | 2.11 | 0.76 | 20.8 |
| Nps_3 #10 | Outer ont. | 2.38 | 0.76 | 20.4 |
| Nps_3 #11 | Outer ont. | 2.58 | 0.76 | 19.9 |
| Nps_3 #12 | Outer ont. | 1.84 | 0.76 | 20.2 |
| Multi-net MN 37/62; Sample interval 150 – 500 m | | | | |
| Nps_26 #1 | Inner ont. | 2.14 | 0.72 | 19.0 |
| Nps_26 #2 | Inner ont. | 1.09 | 0.72 | 21.1 |
| Nps_26 #3 | Outer ont. | 2.55 | 0.72 | 18.9 |
| Nps_26 #4 | Outer ont. | 1.41 | 0.72 | 17.9 |
| Nps_26 #5 | Outer ont. | 2.85 | 0.72 | 17.0 |
| Nps_26 #6 | Inner ont. | 1.93 | 0.72 | 18.7 |
| Nps_26 #7 | Inner ont. | 2.06 | 0.72 | 19.1 |
| Nps_26 #8 | Outer ont. | 2.36 | 0.72 | 19.0 |
| Nps_26 #9 | Outer ont. | 2.16 | 0.72 | 19.5 |
| Nps_27 #1 | Inner ont. | 2.23 | 0.44 | 18.9 |
| Nps_27 #2 | Inner ont. | 2.32 | 0.44 | 18.4 |
| Nps_27 #3 | Outer ont. | 2.97 | 0.44 | 19.0 |
| Nps_27 #4 | Outer ont. | 2.65 | 0.44 | 18.7 |
| Nps_27 #5 | Inner ont. | 1.96 | 0.44 | 18.7 |
| Nps_27 #6 | Outer ont. | 2.34 | 0.44 | 18.9 |
| Nps_27 #7 | Outer ont. | 2.94 | 0.44 | 19.0 |
| Nps_27 #8 | Outer ont. | 2.28 | 0.44 | 19.7 |
| Nps_27 #9 | Outer ont. | 2.45 | 0.44 | 19.6 |
| Multi-net MN 37/62; Sample interval 500 – 1000 m | | | | |
| Nps_37 #1 | Outer ont. | 2.44 | 0.50 | 18.6 |
| Nps_37 #2 | Outer ont. | 2.34 | 0.50 | 18.9 |
| Nps_37 #3 | Inner ont. | 0.62 | 0.55 | 17.5 |
| Nps_37 #4 | Outer ont. | 2.60 | 0.55 | 19.7 |
| Nps_37 #5 | Outer ont. | 2.33 | 0.55 | 21.1 |
| Nps_37 #6 | Outer ont. | 2.08 | 0.55 | 20.6 |
| Nps_37 #7 | Outer ont. | 2.34 | 0.55 | 20.1 |
| Nps_37 #8 | Outer ont. | 2.44 | 0.55 | 19.7 |

[a] 2 SD of the bracketing standard analyses.

(Wu and Hillaire-Marcel, 1994; Ravelo and Hillaire-Marcel, 2007). In contrast, other authors have classified *N. pachyderma* (sin.) as a deep dweller (Duplessy et al., 1991; Kohfeld et al., 1996; Simstich et al., 2003), implying that sea surface temperature and salinity conditions are not generally recorded in the $\delta^{18}O$ of this foraminiferal species. Based on these observations, the purpose of this study is to shed new light on the existing paleo records of *N. pachyderma* (sin.) by ion microprobe analysis and to assess the limitations of conventional bulk analyses for paleoceanographic applications.

## 2. Material and methods

### 2.1. Samples and preparation

Intratest oxygen isotope analyses were made on the polar to subpolar planktonic foraminifer *N. pachyderma* (sin.) from a Holocene core top (Table 1: samples Nps_43 and Nps_44; core 23528-3, 63.16°N, 28.84°W, 1632 m water depth) and a multi-net station that sampled in October 1995 (Table 1: samples Nps_3 from 0–50 m, Nps_26 and Nps_27 from 150–500 m and Nps_37 from 500–1000 m; multi-net MN 37/62, 75.00°N, 00.35°E) (Fig. 3). These samples were previously described by Jensen (1998) and Simstich et al. (2003). The foraminiferal tests were handpicked, cast with 2 grains of calcite standard, UWC-3, within 5 mm of the center of a 25 mm round epoxy mount, ground to midsection and polished (Fig. 2B). The suitability of chamber wall profiles for ion microprobe analysis was evaluated by backscatter electron imaging (BSE) using a scanning electron microscope (SEM) in variable pressure mode. At this stage, the epoxy mounts were not coated in order to estimate the porosity of the foraminiferal tests and to identify samples showing signs of dissolution or contamination. Subsequently, the sample mounts were cleaned and gold coated.

### 2.2. Calcite standard UWC-3

The reference material used in this study is the new calcite standard, UWC-3, that was derived from a granulite facies diopside bearing calcite marble from the Adirondack Mountains of New York (sample # 95AK24, Edwards and Valley, 1998). The chemical characterization of UWC-3 standard was performed by 69 electron microprobe measurements in 10 calcite grains (supplementary data, Table D1). The UWC-3 calcite standard contains 5450 ppm of Mg (±410 ppm 1 SD), 4050 ppm of Fe (±950 ppm 1 SD), 1220 ppm of Mn (±690 ppm 1 SD), and an average concentration of 2230 ppm Sr (semiquantitative, close to detection limit). The concentration of Ba is low but variable and averages at 1230 ppm.

UWC-3 was analyzed by standard phosphoric acid techniques in the Stable Isotope Laboratory, Dept. of Geology & Geophysics, University of Wisconsin-Madison. Values of $\delta^{18}O$ are reported relative to accepted values for NBS-19. The $\delta^{18}O_{(SMOW)}$ of UWC-3 is 12.49‰ (±0.03‰ 1 SD, $n=9$) and the $\delta^{13}C_{(PDB)}$ is −0.91‰ (±0.04‰ 1 SD, $n=9$) (supplementary data, Table D2).

### 2.3. Ion microprobe oxygen isotope analyses

Oxygen isotope analyses were performed on the Wisc-SIMS CAMECA ims-1280 high resolution, multi-collector ion microprobe at the University of Wisconsin-Madison using a $^{133}Cs^+$ primary ion beam with an intensity of 15 to 18 pA, which was focused to a size of approximately 2×3 μm (session 1, 2) and 4×6 μm (session 3), forming analysis spots with a depth of 3 to 4 μm. General conditions of the analyses are similar to those in Page et al. (2007) who used sub-μm primary spots. The secondary $O^-$ ions were detected simultaneously by a Faraday cup ($^{16}O^-$) and a miniaturized Hamamatsu electron multiplier ($^{18}O^-$). The count rates were 1.3 to $2.1\times10^7$ cps and 2.7 to $4.6\times10^4$ cps for $^{16}O^-$ and $^{18}O^-$, respectively. Total analytical time per spot was about 20 min including pre-sputtering (5 min), automatic centering of the secondary ion image (ca. 2 min), and analysis (ca. 13 min). The base line noise level of the Faraday cup was monitored during the pre-sputtering.

Grains of UWC-3 that were mounted in the center of each sample were measured in at least four spots before and after every 6 to 8 foraminiferal sample analyses, and the resulting average value bracketing the samples was used for instrumental mass fractionation (IMF) correction. Reproducibility of the individual spot analyses of UWC-3 standard (bracketing samples) is assigned as uncertainty of unknown samples, and varies from 0.44 to 0.76‰ (2 SD). A total of 103 analyses were performed including 63 UWC-3 measurements bracketing the samples. Furthermore, additional measurements were performed on UWC-3 to determine the minimum distance between sample spots without degrading precision, which was found to be 5 μm (Fig. D1, supplementary data).

After ion microprobe measurements, the appearance and location of analysis spots were imaged by SEM (Figs. D2–D20, supplementary data). Oxygen isotope data from spots overlapping epoxy resin, foraminiferal growth boundaries, or chamber walls with areas of high porosity were discarded (Table D3, supplementary data).

The distribution of Mg in foraminiferal chamber walls is variable (e.g. Eggins et al., 2004; Sadekov et al., 2005). This has to be taken into consideration as the difference in IMF for $\delta^{18}O$ in calcite and dolomite $\Delta_{IMF}$(Cal–Dol) amounts to 5.5‰ using standard procedures at Wisc-SIMS (Bowman et al., 2008). In an electron microprobe study on core top tests of *N. pachyderma* (sin.), Nürnberg (1995) found an intratest range in Mg of 30 to 1100 ppm ($n=531$), which is in good agreement to later studies of Eggins et al. (2004) and Kunioka et al. (2006). Therefore, the heterogeneity of Mg in foraminiferal tests corresponds to a maximum bias in measured $\delta^{18}O$ of 0.05‰. The UWC-3 standard contains 5450 ppm of Mg (±410 ppm 1 SD, $n=69$, $X_{Mg}=0.024$; supplementary data, Table D1), corresponding to a bias of 0.26‰ in measured $\delta^{18}O$. Depending on the Mg content of the foraminiferal test at spot location, the cumulative difference in IMF varies between 0.21% and 0.26% and is therefore significantly smaller than the analytical precision achieved in this study. Consequently, no matrix effect correction was applied.

### 2.4. Calculation of equilibrium $\delta^{18}O$ profiles

Temperature and salinity data for the months of July to September, which characterize the main planktonic bloom in the Northern North Atlantic (Kohfeld et al., 1996; Jensen, 1998; Schröder-Ritzrau et al., 2001), were extracted with a vertical resolution of 25 m from the hydrographic database, 'World Data Atlas 2001' (Conkright et al., 2002; supplementary data, Table D4), using the software 'Ocean Data View' (Schlitzer, 2007). The $^{14}C$ ages of 23 adjacent core top samples from the northern North Atlantic are published in Simstich et al. (2003) and represent the Latest Holocene. Thus, we correlate the $\delta^{18}O$ values of foraminiferal tests to modern hydrographic data.

The $\delta^{18}O_{(water)}$ values corresponding to the multi-net MN 37/62 samples from the Greenland Sea, northern North Atlantic, were calculated using the $\delta^{18}O_{(water)}$-salinity relationship of Simstich (1999) and Weinelt et al. (2001) deduced from a new set of water profiles specific for the Norwegian and Greenland Sea:

$$\delta^{18}O_{(water)}[‰\,VSMOW] = -12.17 + 0.36\times S \quad (1)$$

where S refers to salinity (in wt.‰). For the core top sample 23528-3, the $\delta^{18}O_{(water)}$-salinity relationship for waters collected in the upper 250 m of the North Atlantic during the GEOSECS expedition (GEOSECS, 1987; Duplessy et al., 1991) was applied:

$$\delta^{18}O_{(water)}[‰\,VSMOW] = -19.264 + 0.558\times S \quad (2)$$

Equilibrium $\delta^{18}O$ values were calculated using the fractionation factor for calcite and water determined by O'Neil et al. (1969):

$$1000\ln\alpha\,(\text{calcite} - H_2O) = 2.78\left(10^6T^{-2}\right) - 3.39 \quad (T \text{ in K}) \quad (3)$$

Most palaeoceanographic studies based on *N. pachyderma* (sin.) still use the equation of O'Neil et al. (1969), however, newer determinations of the $CO_2$-$H_2O$ and the phosphoric acid-$CO_2$ fractionation factors lead to a slightly different calibration of the calcite-water fractionation factor (Kim and O'Neil, 1997). In order to maintain comparability with previous publications, we applied the equation of O'Neil et al. (1969). The difference in equilibrium $\delta^{18}O$ values calculated by the equations of O'Neil et al. (1969) and Kim and O'Neil (1997) is less than 0.3‰ in the relevant temperature range and therefore smaller than the analytical precision achieved in this study.

Oxygen isotope ratios of marine carbonates are commonly expressed relative to PDB. Therefore, a conversion from calcite $\delta^{18}O$ on the VSMOW to the PDB scale was applied using the equation of Coplen et al. (1983):

$$\delta^{18}O[‰\,PDB] = 0.97002 \times \delta^{18}O[‰\,VSMOW] - 29.98 \quad (4)$$

In addition, temperature and salinity data from a Conductivity–Temperature–Depth recorder (CTD) are available for the multi-net station MN 37/62 (Jensen, 1998) from the day of sampling (Oct. 18, 1995). The vertical $\delta^{18}O_{(water)}$ profile was calculated by CTD salinity data and Eq. (1). These values were used in combination with CTD temperature data for the calculation of the equilibrium $\delta^{18}O_{(calcite)}$ profile by Eqs. (3) and (4).

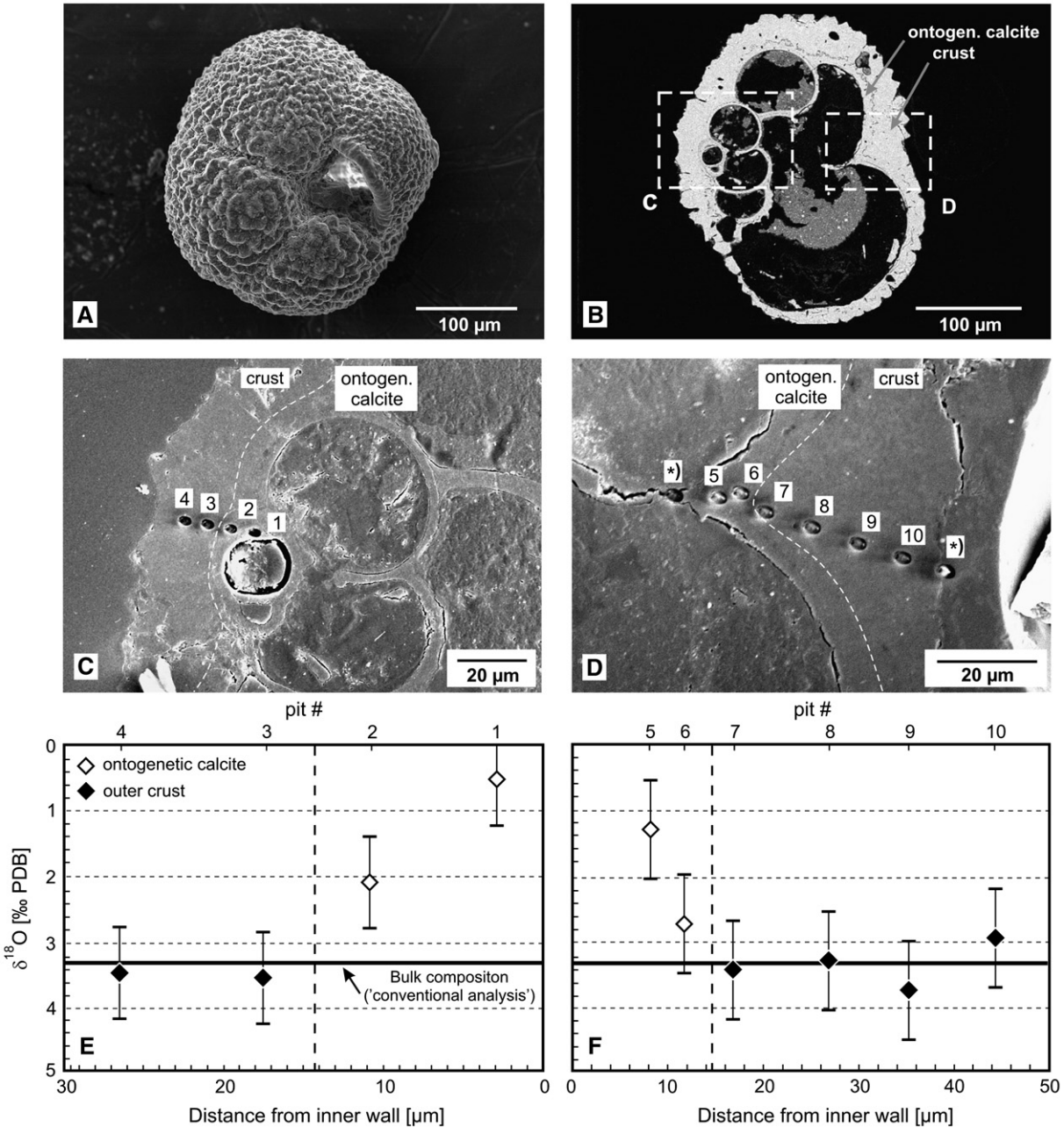


**Fig. 4.** SEM images (A–D) showing an encrusted foraminiferal test (umbilical view) and a polished cross-section from the core top 23528-3 (sample Nps_43 in Table 1). Note that areas filled by epoxy are black in figure B, and dark grey in figures C and D. C) SEM image of the gold-coated sample displaying the ion microprobe spot locations of the traverse in 'C' comprising ontogenetic calcite of early chambers and crust. D) SEM image of the ion microprobe traverse comprising inner layers of the final and penultimate chamber, and outer crust. Ion microprobe pits overlapping the epoxy are indicated with an asterisk. The corresponding $\delta^{18}O$ values (Figs. E, F), that are arranged by distance from the inner chamber wall, vary systematically with their location in the crust and reflect growth history. Error bars represent 2 SD. Conventional 'bulk' data are from Simstich et al. (2003) comprising multiple pooled tests in the same size fraction (125–250 µm) from this sample.

## 3. Results

### 3.1. Intratest oxygen isotope variability in core top N. pachyderma (sin.)

Based on the appearance of the cross-sections after sample preparation, two Holocene tests of *N. pachyderma* (sin.) from the core top 23528-3 (Fig. 3 and Table 1: Nps_43 and Nps_44) were selected out of a group of four mounted specimens for ion microprobe analysis. The maximum diameter of these tests, that are derived from within one centimeter of the seawater interface at the time of sampling and therefore represent the youngest sediments, is 240 and 260 μm. In Nps_43, two traverses were sampled crosscutting foraminiferal chamber walls that comprise both the inner calcite layers (ontogenetic calcite) and the outer calcite crust (Fig. 4). Except for the final chamber, which is less encrusted, the crust contributes more than 70% to the total wall thickness of about 30 to 50 μm (Fig. 4). Values of $\delta^{18}O$ in this Holocene core top sample vary from 0.5‰ to 3.7‰ [PDB] (Table 1). The lowest $\delta^{18}O$ value of 0.5‰ is derived from the inner walls of the smallest exposed chamber, indicating an early juvenile stage. The $\delta^{18}O$ value of the ontogenetic calcite differs significantly from that of the crust. In the ontogenetic layer, oxygen isotope ratios range from $\delta^{18}O$=0.5‰ to 2.7‰ with an average of 1.7‰ ($n$=4) and are significantly lower than $\delta^{18}O$ values of the outer crust, that vary between 3.0‰ and 3.7‰ with an average $\delta^{18}O$ value of 3.5‰ ($n$=7). Hence, the average difference in $\delta^{18}O$ between these two phases of foraminiferal calcite amounts to 1.8‰. Given that the test mass of encrusted *N. pachyderma* (sin.) is 3 to 4 times larger than the nonencrusted forms (Kohfeld et al., 1996), the weight-balanced value of $\delta^{18}O$ of this core top test is 2.9‰. Ion microprobe measurements of Nps_44 from the same core top revealed a remarkably consistent distribution of the intratest oxygen isotope variations (Table 1). Two measurements in the ontogenetic calcite layers show values of 1.4 and 1.8‰, whereas $\delta^{18}O$ in the crust ranges from 3.6 to 3.9‰ ($n$=3). The difference between these two types of calcite is 2.1‰, and the weight-balanced 'bulk' $\delta^{18}O$ of the whole test is 3.1‰, assuming that the crust contributes to about 70% to the total test weight. Therefore, the estimated bulk $\delta^{18}O$ of Nps_43 and Nps_44 based on ion microprobe measurements is consistent with the bulk value of $\delta^{18}O$=3.3‰ for multiple pooled tests of the same species and size fraction from the same sample vial determined by the conventional analysis employing phosphoric acid dissolution of whole tests (Simstich et al., 2003). Thus, the new ion microprobe data reveal a significant and consistent difference of about 2‰ between the two generations of calcite. Furthermore, calculated bulk values for each foraminiferal test agree within analytical uncertainty with conventional bulk data from much larger samples.

It is known from previous studies that the ontogenetic calcite in planktonic foraminifera is precipitated in the euphotic zone above the pycnocline (upper 100 to 150 m) whereas the calcite crust is deposited in colder waters at depths of at least 200 m (Bé, 1980; Duplessy et al., 1981; Arikawa, 1983; Kohfeld et al., 1996; Stangeew, 2001). According to these habitat preferences, ion microprobe data for the core top samples are compared to equilibrium $\delta^{18}O$ profiles (Fig. 5) for the summer months, July to September, reflecting the major production spike in this region (Kohfeld et al., 1996; Jensen, 1998; Schröder-Ritzrau et al., 2001). This comparison reveals that the total range of about 3‰ in $\delta^{18}O$ within a single foraminiferal test exceeds the variability in the $\delta^{18}O$ profile of calcite in equilibrium with the water column by a factor of three.

### 3.2. Intratest oxygen isotope variability in net catches

To verify the core top data and to eliminate any possible bias due to sample contamination, dissolution, or diagenetic alteration, additional ion microprobe measurements were performed on net sampled *N. pachyderma* (sin.) from different depth intervals (multi-net MN 37/62, 75.00°N, 0.35°E, Greenland Sea, Fig. 3). The multi-net was

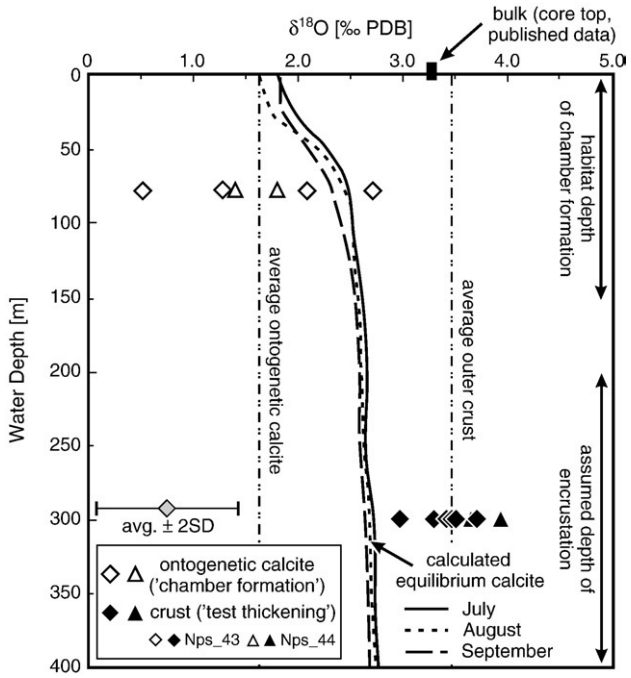


**Fig. 5.** Oxygen isotope values of 2 to 6 μm spots in the ontogenetic calcite and the outer crust measured in two individual tests of core top *N. pachyderma* (sin.) from the North Atlantic (core 23528-3 in Fig. 3; Nps_43 and Nps_44 in Table 1) plotted against water depth and the calculated equilibrium calcite profiles from July to September (main planktonic bloom) at core location. The approximate depth intervals for chamber formation and encrustation were chosen according to plankton tow studies (Stangeew, 2001). The oxygen isotope ratios of the crust match published 'whole test' data from bulk foraminiferal analysis, indicating a high degree of test encrustation at this core location.

equipped with five net bags that were opened and closed individually, providing the capability to sample discrete depth intervals during vertical lifting. Further information about the sample material and the method of sampling are provided in Jensen (1998). A total of four individual tests were analyzed, covering the depth intervals 0–50 m (Nps_3), 150–500 m (Nps_26 and Nps_27), and 500–1000 m (Nps_37). In contrast to core top samples, the tests of net sampled foraminifera are smaller and nonencrusted, indicating that their life cycle is incomplete (Fig. 6). Therefore, the average wall thickness amounts to only 10–20 μm. As there were few suitable locations for crosscutting traverses due to cracks and internal crust features seen by SEM, the study of these samples was mainly focused on the difference in $\delta^{18}O$ of the inner and outer ontogenetic calcite layers. The oxygen isotope ratios in the four tests show a significant trend towards higher values from the inner to the outer ontogenetic crust with the highest range within a single test of 2‰ (the example of Nps_3 is shown in Fig. 6, all data in Fig. 7 and Table 1). Values of $\delta^{18}O$ within the inner ontogenetic calcite layers in four individual tests vary from 1.1‰ to 2.3‰ [PDB] with an average of 1.7‰ ($n$=12). One anomalously light value of 0.6‰ was found in Nps_37 from the depth interval 500–1000 m. In the outer ontogenetic layers, $\delta^{18}O$ values vary between 1.4 and 3.0‰ with an average of 2.4‰ ($n$=26). Hence, the average difference in $\delta^{18}O$ between the inner and outer ontogenetic calcite layers amounts to 0.7‰. The total intra-ontogenetic range of $\delta^{18}O$ in net sampled specimens varies from 1.4‰ in the sample interval 0–50 m to 2‰ in the sample interval 500–1000 m which is comparable to the intra-ontogenetic range of 1.5‰ from the inner to the outer ontogenetic layers in the core top sample NPS_43. It is notable that the average oxygen isotopic ratios of net sampled specimens from different depth intervals do not reflect the changes of equilibrium $\delta^{18}O$ values with water depth, implying that the depth interval of sampling does not necessarily reflect the water depth of chamber formation. Similar to the ontogenetic calcite in the core top samples, average oxygen isotope ratios in net sampled

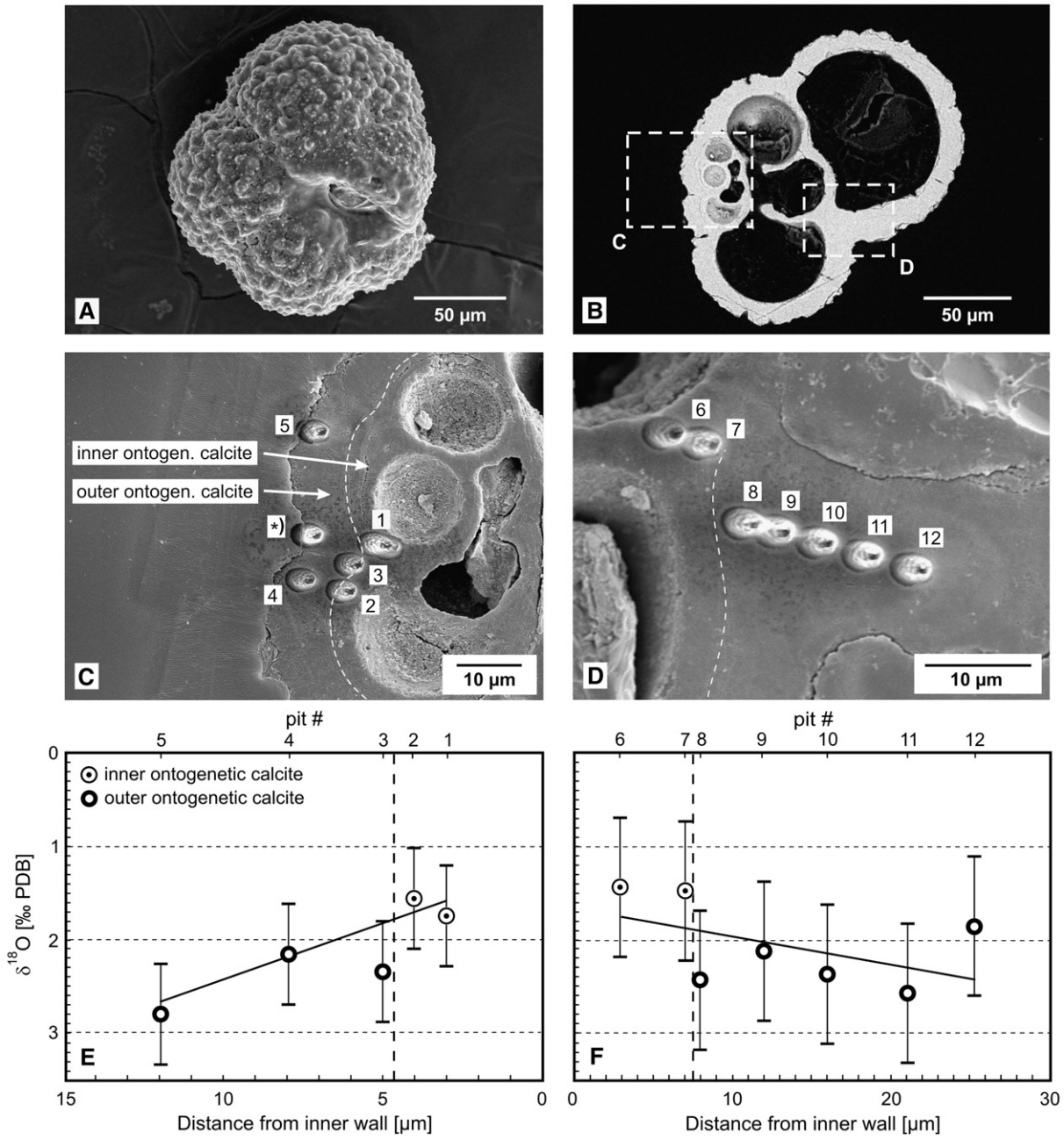


**Fig. 6.** SEM images (A, B) showing a nonencrusted foraminiferal test (umbilical view) and a polished cross-section (NPS_3 in Table 1) sampled by a multi-net (MN 37/62, Fig. 3) in the depth interval 0–50 m. Note the difference in size and wall thickness in comparison to the core top sample (Fig. 4; different scale). C) SEM image of the gold-coated sample showing the ~3 µm ion microprobe spot locations on the inner and outer layers of juvenile chambers. The ion microprobe pit overlapping epoxy is indicated with an asterisk. D) SEM image of the ion microprobe traverse comprising inner and outer layers of the final chamber. Encrustation does not occur in this early life stage, therefore, both the inner and outer calcite layers in this figure correspond to the 'ontogenetic layer' shown in Fig. 4 E, F). The corresponding $\delta^{18}O$ values are arranged by distance from the inner chamber wall. Error bars represent 2 SD. Due to the small amount of sample material, $\delta^{18}O$ values by bulk analysis are not available for this sample.

specimens exhibit a negative fractionation of about −1‰ relative to equilibrium $\delta^{18}O$ values in the euphotic zone above the pycnocline (upper 100 to 150 m, Fig. 7).

## 4. Discussion

### 4.1. Deviations of foraminiferal $\delta^{18}O$ from equilibrium

Various studies have reported deviations of the $\delta^{18}O$ values in foraminiferal tests from those expected for inorganic calcite precipitated in thermodynamic equilibrium with ambient seawater, (cf. Rohling and Cooke, 2002). This 'apparent' vital effect, $\Delta^{18}O_{(M-E)}=\delta^{18}O_{(measured)}-\delta^{18}O_{(equilibrium)}$, is widely interpreted to be species specific and to result from biologically mediated precipitation in disequilibrium with ambient seawater (Urey et al., 1951; Wefer and Berger, 1991). Unfortunately, neither accurate nor precise estimation of foraminiferal vital effects has been possible previously because the depths of ontogenetic chamber formation and subsequent encrustation are preconditioned by the stratification of the water column, which is highly variable (Simstich et al., 2003). *N. pachyderma* (sin.) inhabits the euphotic zone above the pycnocline (0 to about 150 m) during the ontogenetic development, whereas the final encrustation predominantly reflects water depths below about 200 m (e.g. Srinivasan and Kennett, 1974; Kohfeld et al., 1996; Norris et al., 1998; Stangeew, 2001).

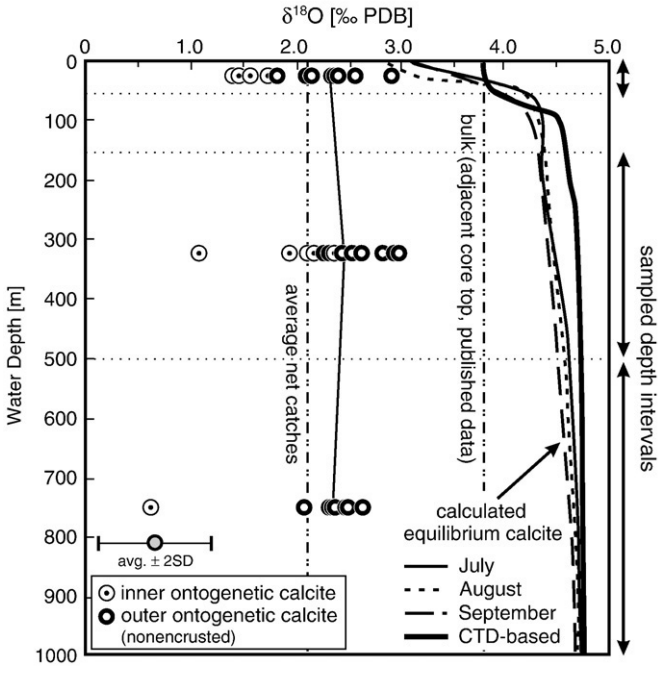


**Fig. 7.** Oxygen isotope values of ~3 μm spots in four *N. pachyderma* (sin.) tests from multi-net station MN 37/62 from the Greenland Sea (Fig. 3) plotted according to the sampled depth intervals. The equilibrium profiles represent the months July to September (main planktonic bloom), supplemented by an equilibrium profile based on data from a Conductivity–Temperature–Depth recorder (CTD) derived from the day of sampling (Oct. 18, 1995). Equilibrium profiles were calculated after O'Neil et al. (1969). All values of $\delta^{18}O$ from the inner ontogenetic calcite layers are negatively fractionated relative to equilibrium with ambient seawater. Published core top data from a nearby station are shown for comparison (core top PS2613; Simstich et al., 2003).

Consequently, calculation of an accurate foraminiferal vital effect based on a single equilibrium $\delta^{18}O$ value is not possible. For this reason, ion microprobe $\delta^{18}O$ measurements from the ontogenetic layers and the outer crust of the two core top samples are plotted against apparent temperatures assuming equilibrium with ambient seawater (Fig. 8). The range of intratest oxygen isotope values in the foraminiferal tests exceeds the range of equilibrium $\delta^{18}O$ by a factor of about three. Only two $\delta^{18}O$ values from the ontogenetic calcite and none from the crust potentially reflect equilibrium precipitation.

The largest negative vital effect measured in a core top sample is associated with the smallest chambers exposed in the foraminiferal cross-section (Fig. 4). Furthermore, almost all $\delta^{18}O$ measurements in net sampled specimens, which reflect juvenile stages of the organisms' development, exhibit a large negative vital effect (Fig. 7). This trend confirms earlier studies of Spero and Lea (1996) who used a surgical scalpel blade to amputate chambers of cultured tests of the planktonic foraminiferal species *Globigerina bulloides* for $\delta^{18}O$ measurements. For pooled and homogenized chambers of two different sample groups, they reported an average increase in $\delta^{18}O$ of 0.75‰ from the juvenile to the final chamber. Furthermore, Rollion-Bard et al. (2006) assessed the variability of $\delta^{18}O$ in the benthic foraminifera *Amphistegina lobifera* by ion microprobe analyses. They reported low $\delta^{18}O$ ratios in the keel and parts of the knob area that were secreted at earlier stages, with a total intratest $\delta^{18}O$ variability of 2‰.

This biologically mediated disequilibrium fractionation may be partly explained by the higher calcification rate of juvenile foraminifera that requires a higher respiration rate (Berger et al., 1978; Hemleben et al., 1989). The $\delta^{18}O$ value of respired $CO_2$ is lower by approximately 13‰ relative to $CO_2$ equilibrated with ambient seawater (Epstein et al., 1977). Foraminifera secrete their tests from vacuolized and chemically modified seawater. Therefore, a fast calcification rate or a short distance to the calcification site (i.e. small chamber size of juvenile stages) would favor the incorporation of respired $CO_2$ via vacuoles into the foraminiferal calcite before full isotopic equilibrium with ambient seawater has taken place (McConnaughey, 1989; Spero and Lea, 1996). In addition, small chambers reflect an early stage of the organisms' ontogenetic development and are potentially precipitated in shallower waters with higher temperatures and lower salinities. In this respect it is important to emphasize that the mechanism of foraminiferal calcification is not understood in detail and there is a growing body of evidence that several environmental or biologic factors can affect the deviation from equilibrium $\delta^{18}O$ (Rohling and Cooke, 2002; Erez, 2003).

Our data indicate that processes related to the foraminiferal metabolism are likely to contribute to the vital effects as the variation of $\delta^{18}O$ in the ontogenetic calcite of both core top samples and net catches is significantly larger than the range of equilibrium $\delta^{18}O$ (Fig. 8). Therefore, increasing $\delta^{18}O$ values from the juvenile to final chamber cannot be explained by salinity or temperature variations alone and indicate a changing biologically mediated vital effect during ontogenetic growth. This implies a significant correlation between test size and the bulk oxygen isotope composition.

In contrast to the precipitation of ontogenetic calcite, the addition of the thick final crust is rarely observed in cultured specimens under laboratory conditions (Bé, 1980). Consequently, information about the biologic processes involved in crust formation is limited (cf. Rohling and Cooke, 2002). However, the microtexture of encrusted tests is dominated by large euhedral crystals, pointing towards different mechanisms or pathways of biocalcification to secrete this final layer. A positive $\Delta^{18}O_{(M\text{-}E)}$ in the crust of different planktonic foraminiferal species was previously reported (e.g. Duplessy et al., 1981; Bouvier-Soumagnac and Duplessy, 1985; Spero and Lea, 1993; Kroon and Darling, 1995; Simstich et al., 2003; Hillaire-Marcel et al., 2004). In order to explain these findings, some authors invoked the hypothesis of calcification-at-depth (cf. Rohling and Cooke, 2002), assuming that crust formation takes place in depths of up to 800 m in equilibrium with ambient seawater. In contrast, Spero and Lea (1993) concluded that plankton tow studies do not support calcification at great depth. Furthermore, they reported a positive vital effect for bulk values of $\delta^{18}O$ for encrusted planktonic foraminifera that were cultured in seawater with known $\delta^{18}O$ values, indicating biologic control over crust $\delta^{18}O$. However, the cause of the positive $\Delta^{18}O_{(M\text{-}E)}$ in the final crust of planktonic foraminifera is somewhat elusive and the nature of this enrichment is yet to be resolved.

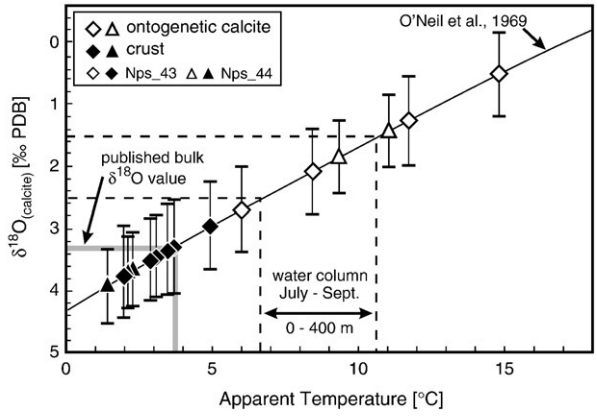


**Fig. 8.** Oxygen isotope values of 2 to 6 μm spots in ontogenetic calcite and outer crust of the two core top tests (core 23528-3, Fig. 3; Nps_43 and Nps_44, Table 1) projected on equilibrium $\delta^{18}O_{(calcite)}$ (O'Neil et al., 1969). The dashed lines indicate the whole range of measured water temperatures and calculated equilibrium $\delta^{18}O_{(calcite)}$ values in the water column during the foraminiferal growth season. Values of $\delta^{18}O_{(water)}$ vary less than 0.1‰ within the water column and the average $\delta^{18}O_{(water)}$ value of 0.3‰ [VSMOW] was used for the calculation of equilibrium $\delta^{18}O_{(calcite)}$. Error bars represent 2 SD. The range of apparent temperatures exceeds the measured range by a factor of three and only two of the analyses represent calcite equilibrated with ambient seawater.

### 4.2. Equilibrium $\delta^{18}O$ estimates

Seawater $\delta^{18}O$ is not unequivocally linked to salinity by a simple linear relation and may be influenced by regional effects of mixing between different riverine and meltwater sources. In this context, the negative vital effect of −1 to −3‰ in net sampled *N. pachyderma* (sin.) from the Arctic Ocean reported by Bauch (1997) was later explained by a possible calcification in high salinity, low $\delta^{18}O$ brines associated with sea ice growth from low salinity surface waters (Ravelo and Hillaire-Marcel, 2007). Hence, in order to avoid these uncertainties, samples for the ion microprobe study were selected from a significantly warmer environment at large distances from the sea ice cover and continental margins. Measured $\delta^{18}O_{(water)}$ profiles adjacent to the core top station do not support the hypothesis of ontogenetic growth in low $\delta^{18}O$ waters (Azetsu-Scott and Tan, 1997). In addition, the North Atlantic relationship between $\delta^{18}O_{(water)}$ and salinity (GEOSECS, 1987; Duplessy et al., 1991, Eq. (2)) is linear with salinities above 34.5‰ characterizing water masses at core location. Similar to that, Simstich (1999) deduced a new relationship between $\delta^{18}O_{(water)}$ and salinity for the Norwegian and Greenland Sea (Eq. (1)) that was applied to calculate equilibrium $\delta^{18}O$ profiles for the multi-net station MN 37/62. This equation is based on 38 water column profiles, some taken adjacent to the station. Again, in the relevant salinity range above 34.5‰, the highest deviation from the linear relationship between salinity and $\delta^{18}O_{(water)}$ is less than ±0.25‰. Consequently, the assumption that *N. pachyderma* (sin.) calcifies in equilibrium with ambient seawater and vital effects are a priori artifacts of local deviations from the linear relationship between $\delta^{18}O_{(water)}$ and salinity (Ravelo and Hillaire-Marcel, 2007) is not supported by seawater $\delta^{18}O$ measurements in close proximity to the sample locations.

### 4.3. The influence of contamination, dissolution or diagenetic overprint

The sensitivity of foraminiferal tests to dissolution depends on the shell microstructure (e.g. surface texture, size and distribution of the pores) and is therefore highly species dependent. In this respect, *N. pachyderma* (sin.) is highly resistant to test dissolution among other planktonic foraminifera (Berger, 1968; Malmgren, 1983). Furthermore, our core was sampled at 1632 m water depth which is well above the Holocene lysocline of ~4900 m in the North Atlantic (Broecker and Takahashi, 1978). Therefore, it is unlikely that the core top samples of this study are affected by dissolution. In general, the sensitivity of foraminiferal $\delta^{18}O$ values to test dissolution is very low. For the foraminiferal species *N. pachyderma* (sin.), Hönisch (2002) reported an increase in bulk $\delta^{18}O$ of less than 0.3‰ after 80 wt.% of the foraminiferal tests were dissolved.

Several processes may alter the original chemical composition of foraminiferal tests after deposition, mainly by the addition of post-mortem diagenetic phases (Boyle, 1981, 1983). Inorganic calcite contains about an order of magnitude more Mg than foraminiferal calcite (e.g. Katz, 1973; Mucci, 1987), therefore, elevated Mg/Ca ratios are an indicator of diagenetic alteration. However, Nürnberg (1995) and Meland et al. (2006) found no aberrant Mg/Ca ratios in *N. pachyderma* (sin.) from North Atlantic core tops using electron microprobe and bulk ICP-OES measurements. Furthermore, most contaminating or diagenetic phases adhere to the outer surface of foraminiferal tests whereas ion microprobe measurements were carried out in the interior of the solid phase. For these reasons, the influence of contamination, dissolution or diagenetic overprint is negligible.

### 4.4. Assessing 'apparent' foraminiferal vital effects by mass balance

Based on the new set of ion microprobe data and reports from previous publications, the over 4‰ range of 'apparent' vital effects, $\Delta^{18}O_{(M\text{-}E)}$, reported for this foraminiferal species (Fig. 1) can be assessed by a simple mass balance calculation. Fig. 9 is the schematic view of the change of $\Delta^{18}O_{(M\text{-}E)}$ in bulk foraminiferal tests throughout their life cycle, deduced from results of the intratest oxygen isotope analyses. The

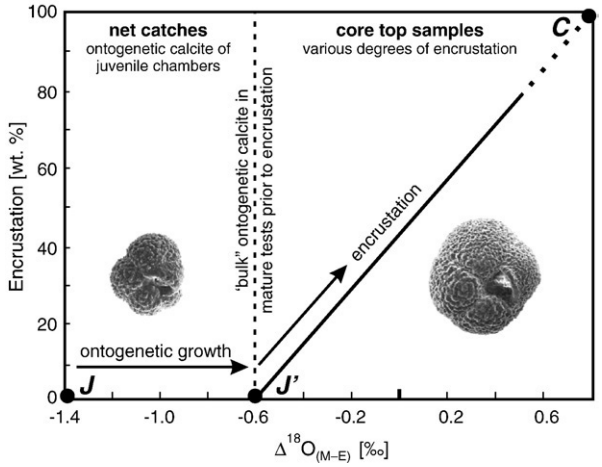


**Fig. 9.** Relationship between the degree of encrustation and the 'apparent' vital effect, $\Delta^{18}O_{(M\text{-}E)}=\delta^{18}O_{(measured)}-\delta^{18}O_{(equilibrium)}$, of bulk foraminiferal tests, based on ion microprobe data for $\delta^{18}O$ in ontogenetic calcite and crust. The intermediate value ***J′*** (juvenile) reflects no encrustation (100% ontogenetic calcite) with a $\Delta^{18}O_{(M\text{-}E)}$ of −0.6‰. This is the average offset between all measurements in the ontogenetic calcite layers of mature core top samples and the average equilibrium $\delta^{18}O_{(calcite)}$ in the euphotic zone above the pycnocline (0–150 m, Fig. 5). Endmember ***C*** (crust) reflects (hypothetical) 100 wt.% encrustation with a $\Delta^{18}O_{(M\text{-}E)}$ of +0.8‰ (Fig. 5). The $\Delta^{18}O_{(M\text{-}E)}$ of up to −1.4‰ (endmember ***J***) is approached by some juvenile chambers and net catches. During ontogenetic growth prior encrustation, chamber $\delta^{18}O$ values increase and hence the vital effect decreases with increasing chamber size, shifting the whole test $\delta^{18}O$ value from *J* to *J′*.

endmember ***J*** represents the negative $\Delta^{18}O_{(M\text{-}E)}$ of −1.4‰ measured in first grown chambers of core top samples and net catches, and ***J′*** indicates the negative $\Delta^{18}O_{(M\text{-}E)}$ of −0.6‰ of the whole mature test prior encrustation. The crust with a positive $\Delta^{18}O_{(M\text{-}E)}$ of 0.8‰ is described by ***C***, which is a hypothetical endmember (100wt.% encrustation). As a consequence of these two counterbalancing vital effects, the single 'whole test' $\delta^{18}O$ value derived by conventional analytical approaches is highly sensitive to the degree of encrustation, and to a lesser extent to the early life history. Hence, variations in the degree of encrustation alone could shift the 'apparent' whole test vital effect $\Delta^{18}O_{(M\text{-}E)}$ from −0.6‰ (***J′*** in Fig. 9) for nonencrusted samples to +0.6‰, assuming an encrustation of about 80 wt.% as reported by Kohfeld et al. (1996). A correlation between test weight and $\delta^{18}O$ with the less encrusted specimens having lower isotopic compositions was previously reported by Hillaire-Marcel et al. (2004).

During the organisms' ontogenetic growth, chamber $\delta^{18}O$ values increase in every newly secreted chamber, shifting the whole test $\delta^{18}O$ from ***J*** to ***J′***. Consequently, the apparent vital effect of encrusted tests is a combination of varying vital effects during ontogenetic growth and variable proportions of the ontogenetic calcite and crust. The $\Delta^{18}O_{(M\text{-}E)}$ values of the ontogenetic calcite are in excellent agreement to previous studies. Bauch (1997) reported disequilibrium 'whole test' values of $\Delta^{18}O_{(M\text{-}E)}$ in the range of about 0 to −2‰ in net sampled *N. pachyderma* (sin.) from the Nansen Basin in the Arctic Ocean (Fig. 1). The large positive vital effects $\Delta^{18}O_{(M\text{-}E)}$ of >0.8‰ that exceed endmember ***C*** (Figs. 1 and 9) can be explained by the fact that in older publications, planktonic 'whole test' $\delta^{18}O_{(calcite)}$ values were often compared to sea surface data (i.e. 0 m water depth) and hence to temperatures, that are significantly higher than the actual conditions at calcification depth.

### 4.5. Interpretation of $\delta^{18}O$ in *N. pachyderma* from paleo records

The ion microprobe data documenting zonation of $\delta^{18}O$ within single foraminiferal tests of *N. pachyderma* (sin.) have significant implications for the understanding of $\delta^{18}O$ records based on this foraminiferal species. Previous studies have shown that the interpretation of bulk $\delta^{18}O$ in *N. pachyderma* (sin.) is challenging. Attenuation as well as amplification of environmental changes was reported based on values of $\delta^{18}O$ for this foraminiferal species (cf. Wu

and Hillaire-Marcel, 1994). In a downcore study comparing two independent proxies, Bond et al. (1993) found that a shift in the abundance of *N. pachyderma* (sin.) from 80% to 100%, suggesting a temperature decrease of at least 6 °C (Imbrie and Kipp, 1971; CLIMAP, 1981), is accompanied by foraminiferal $\delta^{18}O$ values that suggest little or no change in temperature. This enigma could be explained by an increase of higher $\delta^{18}O$ encrustation at lower temperatures and possibly a change in vital effects in comparison to tests measured here that came from warmer waters.

The oxygen isotope variability within single foraminiferal tests now sheds new light on the aberrant proxy signals found in paleoclimate records based on *N. pachyderma* (sin.). The difference in $\delta^{18}O$ measured between the ontogenetic calcite and the crust in this foraminiferal species can be over 3‰. These two generations of calcite are precipitated with vital effects that are opposite in sign and therefore only partly reflect the water column profiles of calcite equilibrated with ambient seawater. Consequently, whole test values of $\delta^{18}O$ are highly sensitive to the actual degree of encrustation or the distribution between early ontogenetic calcite and crust (Fig. 9). As a result, bulk $\delta^{18}O$ data can vary independently of changes in water temperature and salinity, and should be evaluated carefully.

### 4.6. Implications on N. pachyderma morphotypes

The direct comparison of net sampled *N. pachyderma* (sin.) with core top sediment samples is problematic. As first reported by Cifelli (1973) and later confirmed by Arikawa (1983) and Kohfeld et al. (1996), *N. pachyderma* tests from core top sediments are predominantly encrusted to various degrees, whereas encrustation is almost absent in plankton tows and sediment traps from the euphotic zone (0 to approx. 150 m water depth). Duplessy et al. (1981) made a similar observation on different planktonic foraminiferal species and hypothesized that only the thicker-walled tests are preserved in ocean floor sediments. This idea was invoked again by Kohfeld et al. (1996) with the hypothesis that nonencrusted and encrusted specimens potentially represent two different morphotypes. However, a direct comparison between the oxygen isotope data from core top samples and net catches reveals that the existence of two morphotypes is unlikely. The ontogenetic calcite layers of both groups show an identical negative $\Delta^{18}O_{(M\text{-}E)}$, indicating similar habitat preferences for chamber formation and hence for their whole ontogenetic development. Consequently, both core top and net catch samples likely represent the same morphotype in different stages of maturation.

## 5. Conclusions

We determined intratest oxygen isotope variations using multi-collector ion microprobe at 2 to 6 μm spatial resolution in single planktonic foraminiferal tests. This is the first report describing detailed high precision oxygen isotope profiles across the thin calcite layers. We found that the intratest $\delta^{18}O$ variations in the planktonic foraminifera *N. pachyderma* (sin.) exceed the range of the equilibrium $\delta^{18}O_{(calcite)}$ values in the specimens' habitat by a factor of three.

A chamber wall cross-section comprising juvenile chambers as well as the outer crust reveals a total $\delta^{18}O$ range of 3.2‰ within single tests. Values within the inner ontogenetic layers record a time series of the growth history of the foraminiferal test that can only be read by high-resolution ion microprobe analysis. The average isotopic offset between the ontogenetic calcite and the crust is as high as 2.1‰. Both the ontogenetic calcite and the crust precipitate in distinct disequilibrium with ambient seawater, resulting in vital effects that are opposite in sign and indicating different pathways of biocalcification. Consequently, small changes in the degree of encrustation shift whole test $\delta^{18}O$ values significantly and can obscure or falsely amplify environmental signals. Intra-test variability is the main challenge for the interpretation of paleorecords of this high-latitude foraminiferal species and the primary cause of the large range of 'apparent' vital effects. Based on the new ion microprobe data, these apparent vital effects can be explained by a simple mass balance calculation of the two types of calcite.

The ion microprobe data in this study on planktonic foraminifera highlight the potential of this approach for interpreting proxies that are based on living organisms and show that biomineralization can produce small-scale isotope zonation. This technique will also be important in future studies of samples that are cultured under controlled conditions to elaborate on the various environmental factors beside temperature and salinity that are known to affect foraminiferal vital effects. Ion microprobe studies on marine biominerals open a new world of understanding the biological and chemical origin of proxy signals and hence allow the reassessment of aberrant proxy data in paleoclimatic records.

## Acknowledgments

We are grateful to Mara Weinelt for providing the foraminiferal samples. The work greatly benefited from the careful and experienced sample preparation by Brain Hess. We thank John Fournelle for EPMA measurements and assistance during SEM work. This study was funded by NSF (EAR-0509639) and DOE (93ER14389). Wisc-SIMS is partly supported by NSF-EAR (0319230, 0744079). This paper benefited from the reviews of two anonymous reviewers and editorial handling by Jeremy Fein.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemgeo.2008.10.032.

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